III.D Modeling & Simulation

III.D.1 An Integrated Approach to Modeling and Mitigating SOFC Failure

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Objectives

- To develop and demonstrate the feasibility of an integrated predictive computer-based tool for fuel cell design and reliability/durability analysis;
- To generate new scientific and engineering knowledge to better enable Solid State Energy Conversion Alliance (SECA) Industry Teams to develop reliable, low-cost solid oxide fuel cell (SOFC) power generation systems;
- To create technology breakthroughs to address technical risks and barriers that currently limit achievement of the SECA performance and cost goals for solid oxide fuel cell systems; and
- To transfer new science and technology developed in the project to the SECA Industry Teams.

Approach

- The Georgia Tech team is using a multi-physics modeling approach to collectively characterize the interdependency between structural issues and electrochemical/thermal transport phenomena in order to create high-fidelity thermo-mechanical failure analysis models.
- Experimental data from Oak Ridge National Laboratory (ORNL) will be utilized for model validation, and exploratory studies using these modeling tools will be performed to optimize cell and stack level designs.

Accomplishments

- A global/local analysis scheme was developed and illustrated on a 3D co-flow cell model that allows the integration of thermal/fluid simulation results directly combined with local stress analysis.
- Developed a domain integration formulation to evaluate crack tip parameters for fracture analysis.
- Developed a first-order design criterion for the maximum allowable crack size on the electrolyte/anode interface against delamination.
- Developed a first-order design criterion for the maximum allowable localized heating rate against microcracking in the anode.
- It was experimentally determined using a Fourier transform infrared (FTIR) spectrometer that the electrode (anode made of 40 vol% Ni, 60 vol% 8YSZ and cathode made of Sr-doped lanthanum ferrite) samples appear to be opaque over the entire near- and mid-infrared spectra.
- Experimentally determined the radiative properties of common SOFC electrode and electrolyte materials.

- Developed a general formulation (on a spectral basis) for the analysis of the radiative heat transfer in the optically thin electrolyte of the planer SOFC, and wrote and validated a code for implementation of the formulation.
- Developed constitutive models for creep deformation in reduced Ni/YSZ anodes.

Future Directions

- Develop a suitable constitutive model for viscoelastic behavior in Ni/YSZ cermet anode compositions. Incorporate this model into SOFC stress analyses.
- Develop and demonstrate a suitable finite element analysis (FEA) tool for analysis of fracture failure in the context of various pre-existing flaws within SOFC cells under transient and steady-state operating conditions.
- Develop fracture mechanics-based models for damage accumulation in SOFCs.
- Develop models for thermal shock-induced failure in SOFCs.
- Develop models for transient heating for start-up and cool-down analyses.

Introduction

In this work, the Georgia Tech team will take a multi-physics modeling approach to collectively characterize the interdependency between structural issues and electrochemical/thermal transport phenomena in order to create greater fidelity within thermo-mechanical failure analysis models. Once such models and computational algorithms are developed, they will be implemented into various commercial software codes for analysis and simulation. Software such as FLUENT, Star-CD, Marc, ANSYS, and ABAQUS will be used, as needed, for the purpose of validating the convergence and accuracy of the solutions. In addition, limited experimental tests will be conducted in the Phase II project. These tests will be primarily at the material level to understand materials behavior and to obtain certain materials properties needed in the models. Tests will also be conducted to validate the damage evolution models developed in Phase II.

Georgia Tech's Phase I project has demonstrated the feasibility of simulating thermo-mechanical failure in SOFCs using an integrated approach that takes into account the interdependency between structural issues and electrochemical/thermal transport phenomena. Building upon the success of Phase I, Georgia Tech will further develop and mature the multi-physics modeling approach to a level that can be utilized directly by the SECA Industry Teams.

Realizing the complexity and magnitude of technical challenges associated with modeling and simulating SOFC stack failure, the Georgia Tech team will focus on the specific critical tasks listed below. Computational algorithms and related computer codes for the models developed will be transferred to the SECA Industry Teams directly, as well as to Pacific Northwest National Laboratory (PNNL), the National Energy Technology Laboratory (NETL), and ORNL for integration into the Life Prediction and Structural Modeling Tools under development at these national labs.

Approach

Creep Models for Reduced Ni/YSZ Anodes

The Ni/YSZ anode is a mixture of Ni and yttria-stabilized zirconia (YSZ), or a cermet. Due to NiO reduction, the Ni/YSZ anode also contains a large number of voids, making it a porous cermet. In this complicated microstructure, creep deformation will occur predominately in the Ni phase. However, the creep behavior of the anode will be very different from that of bulk Ni due to the presence of YSZ particles and voids. A constitutive creep law needs to be developed for the anode. In this report, several distributions of Ni and YSZ in the anode are investigated in order to gain better understanding of how creep of Ni in the anode will affect the creep of

the mixture of Ni and YSZ. Based on the theories of micromechanics, it was derived that

$$\dot{\bar{\varepsilon}} = c_N \frac{\mu_N}{\mu}\left[\frac{-3c_Y A \mu_N \mu_Y (1-n_c)t}{2\mu}\exp(-\frac{Q}{RT}) + \left(\frac{\mu^N}{\mu}\bar{\sigma}\right)^{1-n_c}\right]^{\frac{n_c}{1-n_c}}$$

This equation gives the strain rate (relaxation) of the entire Ni/YSZ mixture as a function of the overall effective stress. For Ni, n_c is typically greater than one. Thus, the exponent in the above equation is negative, and the quantity inside the brackets is positive and increases with time. Consequently, $\dot{\bar{\varepsilon}}$ vanishes as time goes to infinity. That means that the overall relaxation will eventually cease.

Radiative Property Characterization

The measurement of transmittance of SOFC materials was carried out on an FTLA 2000-154 (ABB Bomem Inc.) Fourier transform infrared (FTIR) spectrometer. In order to measure the reflectance of the sample, the spectrometer was fitted with a 10 SPEC (Pike Technologies) 10-degree specular reflectance accessory.

Transmittance measurements are conducted by measuring the transmission of a beam of normal incidence through a sample as the wavenumber of the light is varied. An infrared detector measures the intensity of the transmitted beam, and this value is reported as a percentage of the source beam. The reflectance measurements are conducted in a similar manner. However, rather than shining normal and through the sample, the beam of light strikes the sample at 10 degrees from normal incidence and a mirror collects the reflected light. This reflected beam is then passed to the infrared detector, and the ratio of intensities of the reflected light to the source beam is the reflectance of the sample. Optical properties were then obtained for several SOFC materials.

Two-Medium Non-Equilibrium Heat Transfer in Porous Electrodes

The proposed two-equation, thermal non-equilibrium model is derived from conservation of energy in the gas and solid phases:

$$\nabla\cdot\left(\rho\,\vec{V}\,c_p\,T_g\right) = \nabla\cdot\left(k_{g,eff}\,\nabla T_g\right) - h_{sf}a_s\left(T_g - T_s\right) \quad \text{(Gas phase)}$$

$$0 = \nabla\cdot\left(k_{s,eff}\,\nabla T_s\right) + h_{sf}a_s\left(T_g - T_s\right) + \sum \dot{Q}'''_{gen\,i} \quad \text{(Solid phase)}$$

where, h_{sf} is the solid-to-gas-phase heat transfer coefficient, a_s is the specific surface area of the media, and $\dot{Q}'''_{gen}$ represents sources of volumetric heat generation within the solid phase. The magnitude of the difference in local temperatures between the gas and solid phases, $(T_g - T_s)$, is an indicator of how valid the assumption of local thermal equilibrium (LTE) might be. Thus, an order-of-magnitude analysis of the terms in the above equation was performed as a first step.

Effects of Mechanical Damage on Cell Stack's Electrical Performance

The electrochemical impact of a delamination crack (between electrolyte and electrode(s)) is that of an electrochemical obstacle. Specifically, the cracked area is a region through which little to no current is generated or flows. As an initial conservative (i.e., "safety factor") measure for quantifying a crack's impact on current flow, it can be assumed that delamination along the purposely thin electrolyte (on the order of microns) results in corresponding regions of nullified electroactivity and charge transport. Stated differently, the thin electrolyte promotes the approximation that delamination locations are effectively "masked" or "de-activated" locales along the cell. Current must thus be generated and conducted outside of the domains of delamination.

Results

Creep Models for Reduced Ni/YSZ Anodes

A representative cell model is used for the finite element analysis. Periodic boundary conditions are prescribed on all four sides of the cell. In other words, the cell element considered here can be viewed as a representative volume in a complete cell. Considering the symmetry of the structure, one only needs to consider a quarter of the representative cell.

In addition to the elastic properties of the cell materials, the creep properties of the anode, as listed

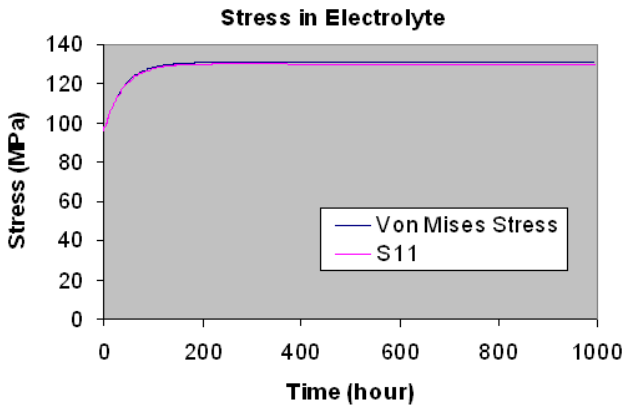

Figure 1. Stress Increment in the Electrolyte Due to Creep in the Anode

in Table 1, are used in the analysis. The electrolyte and cathode are assumed linear elastic without creep.

Table 1. Parameters of Creep Material Model

	A	n_c	Q
Ni/YSZ	$2.0e^{-6}$	1.2	550 kJ/mol

In the analysis, the cell is raised to 800°C rather rapidly. So, creep deformation is neglected during the heating of the cell. Once it reaches 800°C, the cell is kept at this temperature for 1000 hours. Because of creep, stresses in the anode start to relax and approach zero in about 200 hours. Contrary to popular belief, the stress in the electrolyte increases as creep relaxes the stresses in the anode. In the example shown in Figure 1, the in-plane stress in the electrolyte increased by over 30% in about 200 hours. This clearly increases the propensity for electrolyte cracking.

Radiative Property Characterization

Transmittance measurements were used in obtaining the following optical properties for SOFC materials.

Anode (Nickel-doped Yttria-stabilized Zirconia)
Composition: 40% (Ni), 60% ($Zr_{1-x}Y_xO_{2-}$); (vol%) (x = 0.08)
Porosity: 43 vol%
Sample Thickness: 200 m

Cathode (Strontium-doped Lanthanum Ferrite, LSF)
Composition: $(La_{1-x}Sr_x)FeO_{3-}$
Porosity: 24 vol%
Sample Thickness: 200 m

Electrolyte (Yttria-stabilized Zirconia)
Composition: ($Zr_{1-x}Y_xO_{2-}$) (x = 0.08)
Sample Thickness: 330 m

The spectral region of interest for typical SOFC operating conditions (700°C) can be found from Planck's distribution [1], and Murthy and Fedorov [2] showed that 80% of the emissive power is contained within $1.4 < \lambda < 6.1$ m for emission from an object with refractive index n = 1.8. Although data was collected for the spectral range $2 < \lambda < 20$ m, data for $\lambda > 10$ m is of little interest for this application.

For the anode and cathode materials of given thickness, the transmittance measurement was essentially zero within the noise of the FTIR spectrometer (Figure 2). This implies that the absorptive index is very large, i.e. the electrodes are opaque in the mid-infrared region of the electromagnetic spectrum.

For the YSZ electrolyte, the FTIR data shows significant transmittance in the spectral region of interest, indicating that the electrolyte layer of the thickness typically used in SOFCs is optically thin. This transmittance and reflectance data (Figure 3) is used to calculate the absorption coefficient and refractive index as described above. The results of these calculations are shown in Figure 4.

Two-Medium Non-Equilibrium Heat Transfer in Porous Electrodes

An order-of-magnitude analysis of the energy equation for the solid phase of the porous medium was used to estimate the expected temperature difference between the gas and solid phases. This required an estimate of the volumetric heat transfer coefficient between the two phases and an estimate of the volumetric heat generation within the solid phase. The estimated temperature difference based on this analysis was negligible, indicating the validity of the assumption of local thermal equilibrium. Two other criteria found in the

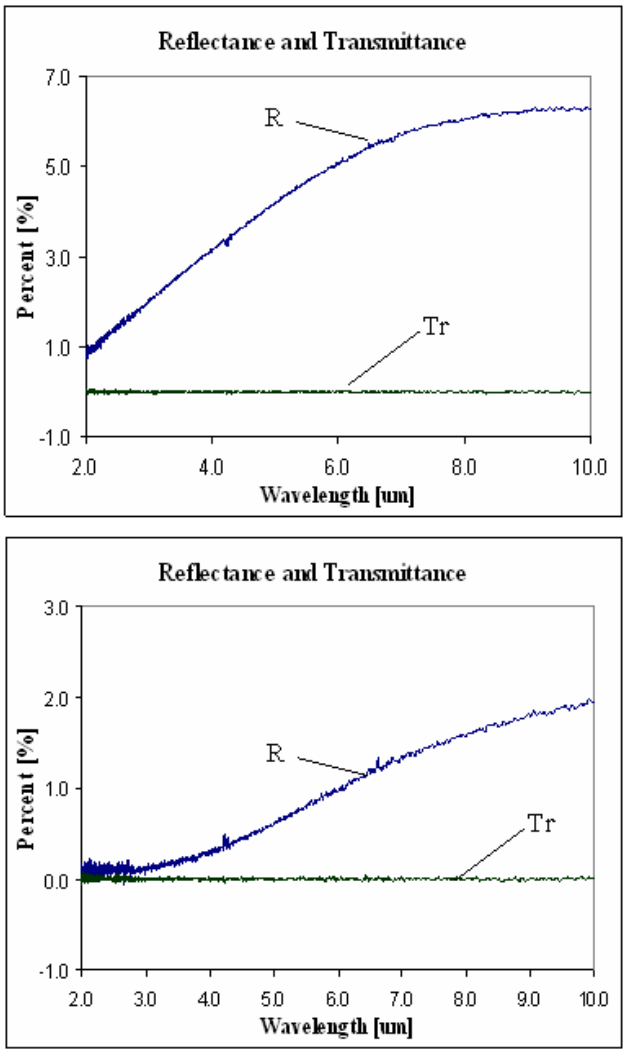

Figure 2. Plots of FTIR Data for LSF (a) and Nickel-doped YSZ (b), Showing Percentage of Reflectance and Transmittance of Samples

literature were applied, and both indicated that local thermal equilibrium in the porous electrodes of SOFCs is probably valid.

However, several critical simplifying assumptions were made concerning the nature of the porous microstructure, the cell operating conditions and heat generation processes, and the magnitude of the current density and heat generation zone. In particular, the local current density (at the microscale level) could be several orders of magnitude greater than the average cell current density depending on the size and distribution of catalytically active sites near the electrolyte/electrode interface.

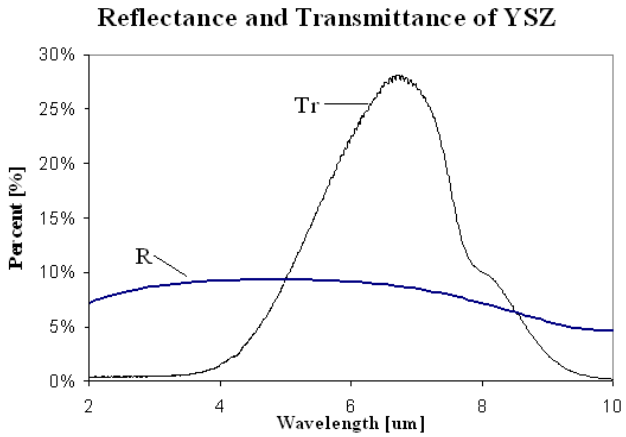

Figure 3. Plot of FTIR Data for YSZ, Showing Percentage of Transmittance and Reflectance

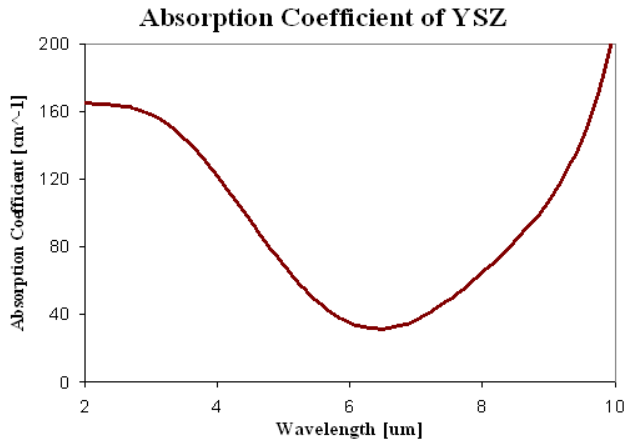

Figure 4. Absorption Coefficient of Electrolyte Material (YSZ)

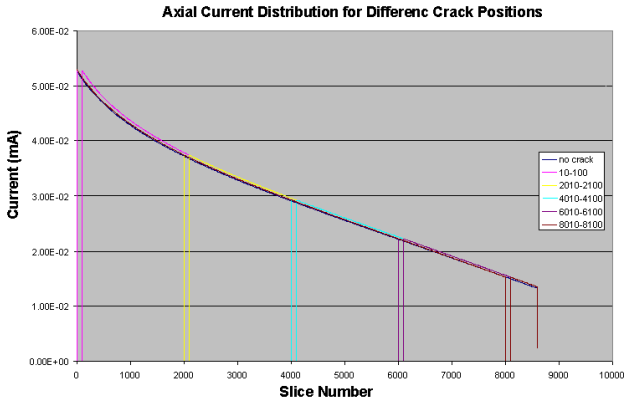

Figure 5. Impact of Crack Location

Effects of Mechanical Damage on Cell Stack's Electrical Performance

A conservative approach, from the standpoint of electrochemical impact of delamination, is the "masking" approximation whereby no current transport is presumed within the SOFC P-E-N segment that is vertically aligned with the delamination zone. In essence, the electroactive region is presumed to be "de-activated" due to separation of the classically considered *plane* of electroactivity, and no *charge transfer* (i.e., current generation) is presumed to occur within such region. Additionally, since the electrolyte thickness is conventionally on the order of microns, there is no in-plane component of ionic current presumed due to exorbitant sheet resistance effects. The result is that the "footprints" of the delamination zones are effectively presumed to become insulated or *"masked"* regions. Such zones are evident within such plots as in Figure 5.

Conclusions

It was experimentally determined using FTIR spectrometer that the electrode (anode made of 40 vol% Ni, 60 vol% 8YSZ and cathode made of Sr-doped lanthanum ferrite) samples appear to be opaque over the entire near- and mid-infrared spectra. The experimentally determined radiative properties of common SOFC electrode and electrolyte materials were made into a material database and delivered to the SECA team. Optical properties such as those obtained here can greatly add to our understanding of heat transfer mechanisms in SOFCs. It has long been debated whether radiation played any role in heat and mass transport in a SOFC environment. Our studies, to a certain extent, have settled that issue.

Additionally, the developed general formulation (on a spectral basis) of the radiative heat transfer in the optically thin electrolyte of the planer SOFC can be used as an effective tool to simulate radiative heat transfer. A software code had been written and validated for implementation of the formulation. The SECA Industry Teams can use this code to analyze radiative heat transfer in their own designs.

Furthermore, the constitutive models developed here for creep deformation in reduced Ni/YSZ anodes enable us to calculate the stress evolution during SOFC operation. Using this model, one can simulate the stresses in the various layers of the SOFC stack as a function of time and temperature. This is a major step toward understanding performance degradation in SOFCs.

References

1. Modest, M., *Radiative Heat Transfer*, 1st Edition, McGraw-Hill, 1993.

2. Murthy, S. and Fedorov, A. G., 2003, "Radiation Heat Transfer Analysis of the Monolith-Type Solid Oxide Fuel Cell", *Journal of Power Sources*, Vol. 124, No. 2, pp. 453-458.

FY 2004 Publications/Presentations

1. Murthy, S. and Fedorov, A. G., 2003, "Radiation Heat Transfer Analysis of the Monolith-Type Solid Oxide Fuel Cell", *Journal of Power Sources*, Vol. 124, No. 2, pp. 453-458.